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WADC TECHNICAL REPORT 54-526

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**DEVELOPMENT OF AN ORGANIC LACQUER
RESISTANT TO FUMING NITRIC ACID**

*FRANCIS J. HONN
ROBERT E. MARTIN
AND
DAVID R. WOLF*

THE M. W. KELLOGG COMPANY

JANUARY 1956

WRIGHT AIR DEVELOPMENT CENTER

WADC TECHNICAL REPORT 54-598

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THE M. W. KELLOGG COMPANY

JANUARY 1956

**PETROLEUM AND CHEMICAL RESEARCH DEPARTMENT
CONTRACT No. AF 33(068)-21258
PROJECT No. 7312
TASK No. 73121**

**WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

**Carpenter Litho & Prtg. Co., Springfield, O.
500 - April 1956**

FOREWORD

This report was prepared by The M. W. Kellogg Company under USAF Contract No. AF 33(038)-21259. The contract was initiated under Project No. 7312, "Finishes and Materials Preservations", Task No. 73121, "Organic Protective Coatings", formerly ND0611-12, "Organic Protective Coatings and Related Materials" and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. Sam Collis acting as project engineer. This report covers work conducted from March 1951 to March 1954.

For the purpose of this report, a number of products were evaluated for a specific application. Many of the materials tested were not developed or intended by the manufacturers for the conditions to which they have been subjected.

Any failure or poor performance of a material is therefore not necessarily indicative of the utility of the material under less stringent conditions or for other applications.

ABSTRACT

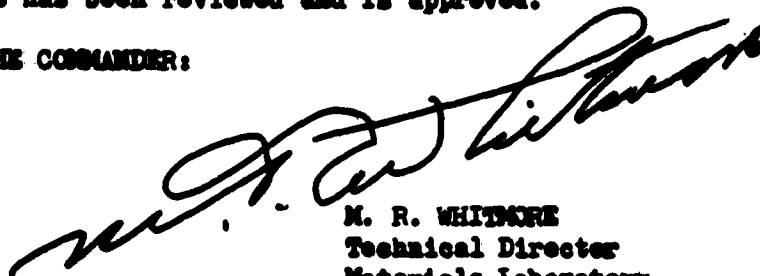
The objective of this contract was the development of a protective coating and sealant for the metal surfaces in the acid tank and ATO compartments of the B-47 aircraft. The evaluation of available coatings indicated that polychlorotrifluoroethylene (KEL-F) was the only organic coating material with adequate resistance to fuming nitric acid. However its use was deemed impractical because of the difficulty of application on aluminum aircraft structures.

Research on the modification of KEL-F through copolymerization with vinylidene fluoride ultimately led to the development of Kellogg X-200 resin. Laboratory tests indicate that coating systems of X-200 filleting material and X-200 lacquer are adequate for the intended application. Coatings formed from the X-200 lacquer are far superior, in fuming nitric acid resistance, to any other lacquer coating evaluated.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITKORE
Technical Director
Materials Laboratory
Directorate of Research

I OBJECTIVE OF CONTRACT

The initial objective of this contract was the development of a "KEL-F" (polychlorotrifluoroethylene) or modified "KEL-F" coating and sealant for the exposed metal surfaces in the acid tank and ATO compartments of the B-47 aircraft. This coating was to be resistant to the penetration of white fuming nitric acid (WFNA), serviceable at temperatures as low as -65°F., and applicable to metal surfaces without adversely affecting their mechanical properties. Later the objective of the contract was expanded to include the protection of vessels, pipes, or other structures which might be exposed to white fuming nitric acid.

II RESEARCH PROGRAM

To attain these objectives, the M. W. Kellogg Company was authorized to conduct an investigation along the following lines:

1. Evaluation of the WFNA resistance and low temperature flexibility of plasticized and unplasticized "KEL-F".
2. Application of "KEL-F" to aircraft aluminum alloys.
3. Development of new fluorine containing resins applicable as air-drying lacquers rather than dispersions requiring high temperature for fusion. This phase of the program included a study of reaction variables in several CF_2-CFCl /fluoro-olefin copolymerization systems.
4. Formulation of lacquers and filleting compounds based on X-200 resin. Much of this work was conducted in cooperation with U.S. Stoneware Company, also WADC contractors. During the latter stages of the contract, Kellogg concentrated on polymerization, U.S. Stoneware on formulation.

III CURRENT STATUS OF THE PROJECT

As of March 31, 1954, the termination date of AF-33(038)-21253, the status of this project is as follows;

1. Although "KEL-F" seems to satisfy the WFNA and low temperature requirements, the dispersion is unsuitable as a protective coating for aircraft aluminum because the high temperatures (480°-525°F.) required for fusion are injurious to the mechanical properties of the aluminum.
2. Of all the soluble lacquer-type coating resins investigated, Kellogg X-200 resin has been selected as outstanding for its resistance to WFNA attack and penetration. This conclusion has been confirmed by an extensive study of coating systems at U.S. Stoneware Company.
3. Formulation of a practical filleting compound based on X-200 resin is close to completion at U.S. Stoneware Company.
4. Formulation of a satisfactory spray lacquer based on X-200 resin is moving ahead satisfactorily at U.S. Stoneware Company, although further work is required on solvent balance and optimum conditions for application and drying.
5. Kellogg has announced the construction of a pilot plant for the manufacture of X-200 resin by early 1955. Meanwhile, Kellogg has promised best efforts to supply Stoneware with enough resin on a procurement basis to keep the formulation program going.
6. Kellogg and Stoneware are cooperating in the development of workable specifications for lacquer grade and filleting compound grade X-200 resin.

IV EXPERIMENTAL DETAILS

EVALUATION OF "KEL-F"

Nitric Acid Resistance of "KEL-F"

"KEL-F" (polychlorotrifluoroethylene) was the first material studied as a nitric acid resistant barrier because of its well-known stability toward strong acids and oxidizing agents.

In making this study it was important to distinguish between chemical attack and penetration. There are some resins, notably polytetrafluoroethylene, which are unattacked by the fuming nitric acids - that is, there is no charring, loss in weight or evidence of molecular scission - yet thin layers of these resins are readily penetrated because they are discontinuous and porous. Properly applied "KEL-F" coatings, on the other hand, are known to be continuous and free from pores, since fusion of successive coats of this true thermoplastic causes the material to flow out into a consolidated barrier. Passage of fuming nitric acid through "KEL-F" would depend, therefore, not on gross leakage through microscopic holes but on diffusion.

The first task was a demonstration of the molecular stability of "KEL-F" on exposure to nitric acid. In one experiment, "KEL-F" resin powder was immersed in WFNA for 50 hours at 125°F. At the end of this period, there was no evidence of charring, decomposition, or decrease in molecular weight. Indeed the solution viscosity of the resin had increased slightly from 2.65 to 2.87 cs /1/. In a second experiment, a compression molded "KEL-F" sheet, 0.060" thick, was immersed in WFNA for 168 hours at 194°F. Again there was no indication of charring, bubbling, or decomposition. The NST /2/ had increased slightly from 325 to 340.

The next step was a demonstration of the dimensional stability of "KEL-F" on exposure to nitric acid. In a series of experiments (Table I), compression molded "KEL-F" strips were immersed for 168 hours in nitric acid at concentrations ranging from 10% to WFNA and at temperatures from 77° to 194°F. Changes in length, width, thickness, and weight of the test strips were very small - generally within experimental error.

The foregoing experiments thus confirm the first of the original contentions - that "KEL-F" is amply resistant to nitric acid attack.

/1/ Solution viscosity of 0.5% (wt.) solution in 2,5-dichlorobenzotrifluoride at 130°C.

/2/ NST = No Strength Temperature, a measure of molecular weight.

TABLE 1
NITRIC ACID RESISTANCE OF "KEL-F"

1. Molecular Stability

KEL-F Sheet, 60 mil, 168 hr. in WFNA at 194°F., MST	<u>Before</u> 325°C.	<u>After</u> 340°C.
KEL-F Powder, 50 hours in WFNA at 125°F., 0.5% viscosity	2.65cs	2.87cs

2. Dimensional Stability

Reagent	Temp.	% Change - 168 hours			
		Length	Width	Thickness	Weight
HNO ₃ -10%	77°F.	-0.03	-0.08	-0.24	0.01
HNO ₃ -conc.	77°F.	0.00	0.00	0.16	0.00
HNO ₃ -conc.	158°F.	-0.77	-0.72	1.55	0.01
HNO ₃ -conc.	176°F.	-1.5	-2.5	0.00	0.00
WFNA	125°F.	-	-	-	0.00
WFNA	194°F.	-	-	-	0.3

3. Pfaudler Tests on Supported Films /1/

a. Unplasticized, amorphous KEL-F on steel

Reagent	Temp.	Film Thickness	Result, Hr.
HNO ₃ -30%	194°F.	5 mil	P-200
WFNA	77°F.	"	P-8128
WFNA	140°F.	"	P-360, F-480
WFNA	194°F.	"	P-225, F-300
WFNA	194°F.	15 mil	P-360, F-480

b. Unplasticized, amorphous KEL-F on aluminum

Reagent	Temp.	Film Thickness	Result, Hr.
WFNA	77°F.	5 mil	P-3408
WFNA	194°F.	"	P-215, F-288

c. Plasticized, amorphous KEL-F on steel

Reagent	Temp.	Film Thickness	Result, Hr.
WFNA	140°F.	5 mil	P-112
WFNA	194°F.	"	F-8

4. WFNA Penetration Tests on unsupported films and sheets

a. Unplasticized, amorphous KEL-F

KEL-F Type	Temp.	Film Thickness	Result, Hr.
Film, Trithene A	70°F.	5 mil	P-1000
" "	125°F.	"	P-125, F-168
" "	"	10 "	P-360
" "	165°F.	"	P-40, F-53
Sheet, pressed	125°F.	15 "	P-1000
" "	165°F.	42 "	P-264

b. Plasticized, amorphous KEL-F

Film, Trithene B	Temp.	Film Thickness	Result, Hr.
" "	70°F.	5 mil	P-125, F-168
" "	"	10 mil	P-180, F-240
" "	125°F.	5 mil	F-5
" "	165°F.	"	F-1

/1/ Note: P-pass, F-fail; if only P is shown, test is still in progress or has been discontinued for reasons of convenience.

The next task was a quantitative determination of the resistance of thin layers of "KEL-F" to nitric acid penetration. Two test methods were employed the Pfaudler cell /1/ for supported "KEL-F" films and a specially-designed glass cell /1/ for unsupported "KEL-F" films and sheets. The results of both series of tests are summarized in Table I.

These data demonstrate clearly the superiority of unplasticized "KEL-F" over the plasticized /2/ form as a nitric acid resistant barrier. For this reason, and because unplasticized "KEL-F" is sufficiently flexible for this application (see below), further study of the plasticized material was abandoned.

In the unplasticized state, "KEL-F" films and sheets seem adequately resistant to WFNA penetration. At 70°F., 0.005" extruded films have been exposed to WFNA for 1000 hours without noticeable penetration. At 125°F., 0.005" films have failed in 168 hours, but 0.010" films have lasted for 360 hours with only slight penetration of WFNA. At 165°F., 0.010" films have failed in 53 hours. But even this performance can be considered good, since few if any other organic coating materials will last for even a fraction of 50 hours at 70°F.

Pressed sheets of unplasticized "KEL-F" are even more resistant to WFNA penetration because of their greater thickness. At 125°F., 0.015" sheets have passed 1000 hours, while at 165°F., 0.042" sheets have lasted 264 hours without failure. How much longer these sheets would have lasted cannot be said, since they seemed to be in excellent condition when the tests were stopped.

Low Temperature Flexibility of "KEL-F"

Although unplasticized "KEL-F" may be classified as a semi-rigid thermoplastic, it is adequately flexible in thin sections to serve as a protective coating or barrier in Air Force applications. After four hours conditioning at -65°F., a 0.010" film was bent 180° around a 1/4" mandrel without cracking. Satisfactory performance at the upper end of the usual Air Force temperature scale (-65° to +160°F.) was assured by the high melting point of this plastic (412°F.).

Application of "KEL-F" to Aluminum Aircraft Structures.

Data in the preceding sections have demonstrated the adequacy of "KEL-F" as a nitric acid resistant barrier over the required temperature range.

/1/ Apparatus and test procedures are described in Appendix A.

/2/ Unplasticized "KEL-F" consists entirely of high molecular polychlorotrifluoroethylene resin. Plasticized "KEL-F" is a blend of the high molecular weight resin with varying amounts (normally 20-25%) of low molecular weight polychlorotrifluoroethylene oils and waxes.

The next practical question was: Can "KEL-F" be applied in some form to the surfaces of the ATO and acid tank compartments of the B-47 aircraft? The complexity of these surfaces (Figures 1,2) made the use of "KEL-F" film ("wall papering") unattractive. Moreover, there is no adhesive known which will firmly bond "KEL-F" directly to metal.

"KEL-F" sheets riveted to the outer walls, floor and ceiling were also ruled out because of the obvious difficulty of sealing the compartments tightly and also because accidental punctures in the sheets would reduce their effectiveness as an acid barrier.

"KEL-F" dispersion coatings thus seemed to be the only practical means of applying a polychlorotrifluoroethylene resin barrier to the compartments. These dispersions (principal grades are N-1, NW-25) consist of fine particles of "KEL-F" resin suspended in volatile organic liquids /1/. They are usually applied by spraying and require fusion at 480°-520°F. for the formation of a continuous film. Since the critical film thickness is 0.0020"-0.0025" per coat, four or five coats are required to build up the 0.010" coating recommended for extreme corrosion protection.

Because certain aluminum alloys deteriorate rapidly at elevated temperatures, tests were conducted on 24S-T3 alclad aluminum alloy exposed to "KEL-F" dispersion fusion conditions. These tests - yield point, tensile strength, and elongation - were divided into three series: (I) Alloy as received; (II) Alloy exposed to four one-hour periods and one five-hour period at 482°F.; and (III) Alloy exposed to four one-hour periods and one five-hour period at 482°F., followed by 12 hours at 375°F. The latter treatment was included as a possible means of restoring the mechanical properties lost during dispersion fusion.

Detailed data are set forth in Table II. The overall effect was an insignificant change in yield point, a 15% loss in tensile strength and a 58% loss in elongation. The 375°F. heat treatment was ineffective. The loss in elongation was considered especially serious - too great to risk in the structural members of the aircraft.

Status of "KEL-F"

In summary:

1. "KEL-F" seems to satisfy the WFMA and low temperature requirements.

2. But "KEL-F" dispersions are unsuitable as a protective coating for aircraft aluminum because the high temperature required for fusion is injurious to the mechanical properties of the aluminum.

/1/ There are no known solvents for "KEL-F" resin at room temperature. Hence, standard type lacquers and paints cannot be made from "KEL-F".

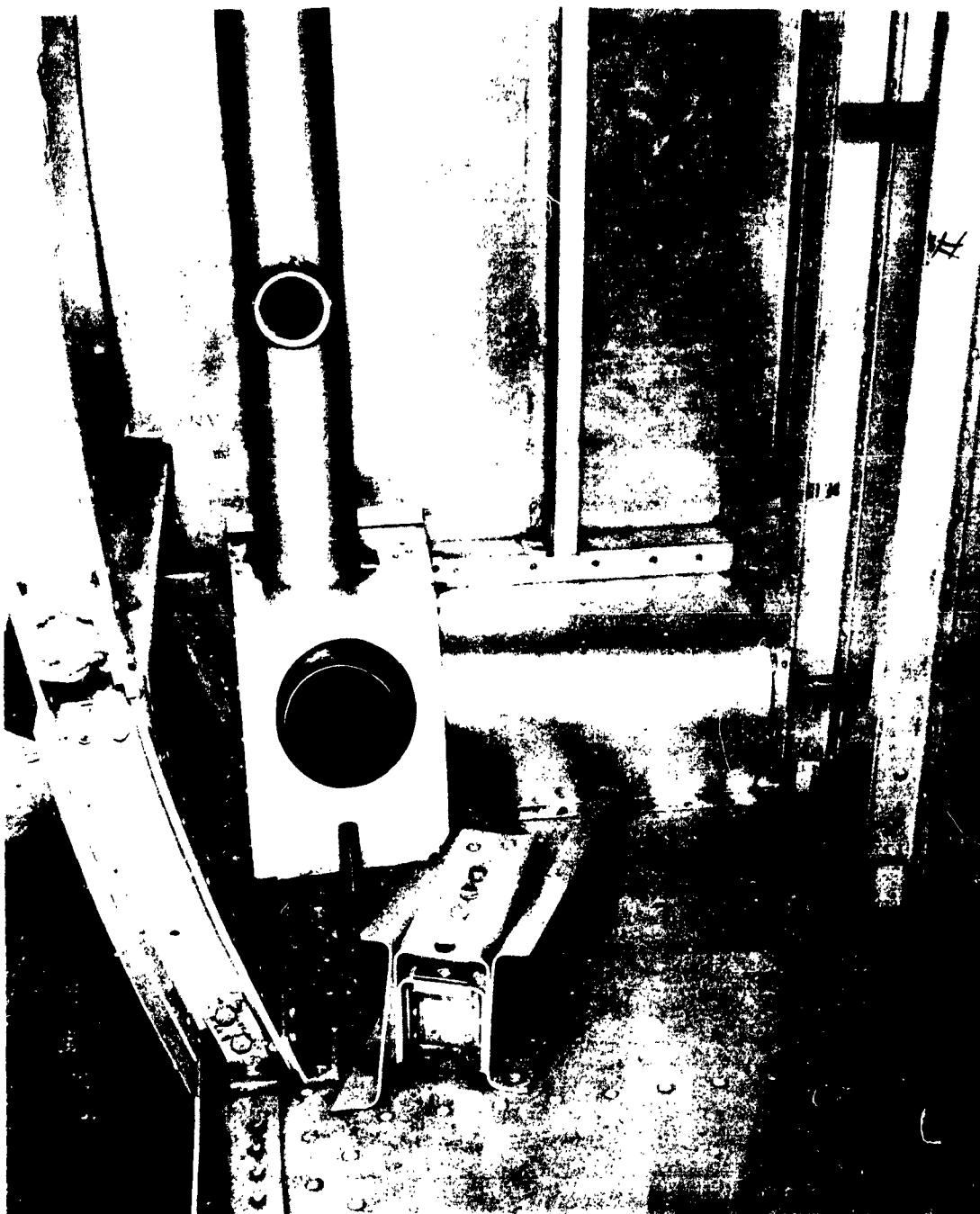


FIG. 1 ATO COMPARTMENT FLOOR



FIG. 2 ATO COMPARTMENT CEILING

WADC TR 54-526

TABLE II

THE EFFECT OF SPRAYED "KEL-F" DISPERSION FUSION
CYCLE ON THE MECHANICAL PROPERTIES OF
24S-T3 ALCLAD ALUMINUM

	No.	Treatment	Yield pt., psi	Tensile Strength, psi	Elongation % in 2-in.
Series I	4	As received	41600	61300	17.5
	8	"	40600	68800	13.5
	7	"	42500	63000	16.5
	av.	"	41600	64400	15.6
Series II	5	(Four 1-hr. cycles	40800	55000	7
	2	(+ 5 hours. at	42300	54200	6
	6	(250°C. (482°F.)	42800	54700	6.5
	av.		42000	54500	6.5
	av. Change, %		+1	-15.4	-58
Series III	1	(Four 1-hr. cycles	42300	54000	6.5
	3	(+ 5 hrs. at	43000	55000	7
	9	(250°C. (482°F.) +	43000	54200	7
	av.	(12 hrs. at 190°C.	42800	54400	6.8
	av. change, %	(375°F.)	+3	-15.5	-56

3. The answer must be sought elsewhere, possibly among certain fluorocarbon resins which are soluble in common solvents at room temperature and are thus capable of being applied to aluminum as air-drying lacquers.

COPOLYMERS OF "KEL-F"

Chlorotrifluoroethylene ($\text{CF}_2=\text{CFCl}$) can be modified by copolymerization with other fluoro-olefins to yield products which are not only thermally stable and chemically inert, but also, in some cases soluble at room temperature in selected organic solvents. Details of the research on these copolymerizations which led to the development of X-200 resin are set forth in Appendix B.

LACQUER FORMULATION

The first lacquers made from X-200 were based upon mass polymerized resin which was dissolved in a mixture of diisobutylketone and ethyl acetate. The solids content of this lacquer was limited to 5% because of the excessively high molecular weight of the resin. When this lacquer was brushed on aluminum and the film air-dried, the adhesion was quite good. The film could not be easily chipped with a fingernail, nor did it tend to peel away from the aluminum.

With the decision to prepare the X-200 resin in a suspension copolymerization system (see Appendix B), the resins obtained were no longer ketone soluble. This was not considered to be too serious a problem, however, since these resins were largely soluble in tetrahydrofuran which is widely used as a solvent for vinyls. Meanwhile, the formulation and testing of various resins for lacquers and sealants at U.S. Stoneware Company, Akron, Ohio, had shown that X-200 was the most promising of all the resins tested as WFNA barriers.

Following a discussion with U.S. Stoneware, it was decided that the next phase of the program should be a concentrated effort to provide several pounds of THF soluble resin to U.S. Stoneware and WADC for formulation. This phase was completed with the shipment of 10 pounds of batch J-4006 to U.S. Stoneware and five pounds of batch J-4015 to WADC.

Lacquer formulation based on this batch, using tetrahydrofuran as a solvent, was not too satisfactory. Good films could be cast from such a lacquer, but sprayed films were rough and pebbly due to the rapid evaporation of the solvent. Incorporation of higher boiling ketones as diluents in the formulation lowered the overall evaporation rate, but such lacquers did not spray well. The ketones were not sufficiently good solvents to prevent the precipitation of resin particles in the partially dried films, thus giving a rough and somewhat porous film.

During this period, the solubility of X-200 in a large number of commercial solvents was determined. The only satisfactory solvents found were cyclic ethers such as tetrahydrofuran, tetrahydropyran, and dioxane. Substituted tetrahydrofurans, which would have been more desirable in view of their high boiling points, were found to be much less effective solvents than THF itself.

It became quite apparent that the best solution to the problem was production of ketone-soluble X-200. Therefore, the major effort here in the Kellogg laboratories was directed toward this goal. This work resulted in several batches which were ketone soluble. Some of this material, designated as batch J-4387, was used for continued lacquer formulation both here and at U.S. Stoneware. Although the viscosity of solutions of this resin was high (14.3% J-4387 solids in a 2/1 mixture of MEK/EEK had a Gardner-Holt viscosity =F), the lacquer could be sprayed by reduction to 11% solids with toluene. Using this lacquer, several unsupported films were prepared for WFNA permeability tests. In Table III, the resistance of some of these films to permeation by WFNA are shown. For comparative purposes, the WFNA permeability of a commercially available, fluorinated lacquer (Nerva-Kote Fluorinax- 39.5% Cl, 30.0% F) is also included.

Two major difficulties still remained in lacquer formulation: (1) It was evident that a balanced solvent system was needed involving enough low boiling solvent to prevent sagging of the coating on vertical surfaces and yet incorporating sufficient amounts of higher boiling solvents to prevent stringing or feathering of the lacquer from the gun. (2) Due to the high solvent retention of X-200 films, a drying schedule was needed that would not promote blistering of the topmost layers of resin. That complete elimination of the solvent from the film was required to obtain maximum resistance is shown by the following resistance measurements made on various films at a potential of 500 volts.

Film	Resistance, megohms at 500 volts, D.C.
5-7 mil, pressed sheet	2.4×10^6
5 mil, air dried, cast film	2.4×10^2
same air dried film after force drying at 95°C. for four hours	4.5×10^4

TABLE III

PERMEABILITY OF X-200 FILMS

NARTS "H" - Cell Test

Film	Thickness Mils	Method of Preparation	Drying Procedure	Days to Failure /1/
J-4411 242-31	11-12	cast in 4 coats from MEK/EHK	air dried	>20 /2/
J-4387 242-24	5-6	sprayed from MEK/EHK	"	>20 /2/
J-4411 242-23	7-8	cast in 8 coats from MEK/EHK	"	>20 /2/
J-4387 242-32-1	3.1	sprayed in 5 coats	"	7 /2/
J-4387 242-32-2	5.0	sprayed in 8 coats	"	>20 /2/
J-4387 242-26B	4.0	sprayed in 2 coats	"	>20 /2/
X-200 J-4411	11-12	cast in 4 coats from MEK/EHK	"	4-5 /3/
X-200 J-4411	7-8	cast in 8 coats from MEK/EHK	"	5-6 /3/
X-200 J-4387	5-6	sprayed from MEK/EHK	"	4 /3/
X-200 J-4387	3-4	cast in 5 coats from MEK/EHK	"	3 /3/
Fluorinax	5	cast in 1 coat	"	5 Hrs. /3/

/1/ Days required for pH on water side of "H" cell to drop to 3.0.

/2/ Merck 90% HNO₃.

/3/ General Chemical propellant grade white fuming nitric acid.

At a joint meeting of U.S. Stoneware, WADC, and Kellogg representatives held on November 2, 1953, it was agreed that X-200 was the only lacquer resin which would fulfill the WFNA resistance requirements of this program. Stoneware and WADC representatives stressed the need for increased amounts of resin for formulation and evaluation. Kellogg representatives agreed and indicated that every effort was being made to make increased amounts of ketone soluble resin available. The two major lacquer formulation problems (as outlined above) were also discussed at this meeting. It was the common belief that the first of these problems could be readily solved and a balanced solvent system established. There were two approaches to the second problem: (1) Work at Kellogg had been based upon air dried films. Table III shows that this work had resulted in a measure of success. Although air dried films were not blistered, the WFNA resistance was lower than was to be expected from X-200 films. (2) The work at U.S. Stoneware had been concerned with force drying of the X-200 films. Although this approach had consistently resulted in blistered films, they were confident that refinement of the forced-drying schedules would produce smooth, solvent free films. Both these approaches had merit since force drying below 300 °F. (149°C.) was acceptable for aluminum structures and would produce films having greater acid resistance within a short time after application, meanwhile air dried films would be the more feasible method of field application and repair. Nor was air drying an impossibility in initial applications since there had been some indication by both WADC and Boeing representatives that the ATO compartments could be coated in production and be air dried for 30 days or even longer before a plane was placed in service.

Following this meeting and during the final months of the Air Force contract with Kellogg, the major emphasis in the Kellogg laboratories was placed upon improvement of the polymerization system with the bulk of the lacquer formulation work being carried out at U.S. Stoneware. This work resulted in several improvements in lacquer formulation. U.S. Stoneware formulation AF-75 was made up:

X-200 (J-4545)	15 parts by weight
"KEL-F" oil 1-3	5
MEK	30
MIBK	30
Toluene	20
	<u>100</u>

This lacquer had a Gardner-Holt viscosity of E and a Ford #4 cup viscosity of 47 seconds. Panels were sprayed with this lacquer and successfully force dried using a graduated forced drying schedule. In addition, Stoneware made up a pigmented lacquer:

X-200	15 parts by weight
"KEL-F" oil 1-3	5
MEK	30
MIBK	30
Toluene	20
Ultron (Zirconium silicate)	20
	<hr/> 120

Pfudler panels were coated with 18 coats of this lacquer (reduced 4:1 with toluene) allowing 15 minutes air dry between coats. These panels were then force dried using the graduated forced drying schedule. The resultant films (11-17 mils) were smooth, blister free, and withstood exposure to WFNA at 125°F. for 67.5 hours before mechanical failure developed in the areas adjacent to the Pfudler gaskets and bushings. The films were otherwise still intact and showed little evidence of chemical attack.

Similar formulations at Kellogg using "KEL-F" powder as a filler were successful. These films were not evaluated due to a shortage of WFNA.

This summarizes the experimental formulation of lacquers up to the termination of this contract. Further formulation at U.S. Stoneware will be primarily concerned with determining the optimum conditions for application and drying. With the production of additional batches of ketone soluble X-200, it is expected that this work will proceed satisfactorily.

SEALANT FORMULATION

Prior to the time that X-200 resin became available for sealant formulation, a compounding study was made using the existing Kellogg resins and oils. The technique employed was to mix the resin particles with the oils or waxes and then to flux the mixture at 135°-150°C. until a homogeneous mass was obtained. The results of this compounding are shown in Table IV. The best putty (formula 5) was examined for performance at -65°F. and at +165°F. Not only did this putty remain soft, elastic, and tacky at -65°F., but it retained these desirable properties to the extent that it could be worked and effectively applied as a filleting material at this low temperature. Nor did this sealant exhibit a tendency to flow or outgas when it was placed in the corner of a slit and folded aluminum panel and exposed at 165°F. for several hours. In addition, the consistency of this putty was such that it could be handled easily in a caulking gun. The main disadvantage of this sealant formula would be the possibility that it would flow excessively at the temperatures encountered in forced drying schedules. However, this point was not checked, and it is conceivable that this difficulty could be precluded by sufficient fluxing of the putty during manufacture. Since this

TABLE IV
EARLY COMPOUNDING OF WFMA RESISTANT SEALANT

Formula	----- Weight Per Cent /1/ -----							Flexibility at -65°F.
	KEL-F Elastomer	/2/	KEL-F-1	KEL-F-3	KEL-F-40	KEL-F-150	Consistency	
1	33	-	67	-	-	-	partly gelled	-
2	-	33	67	-	-	-	firm, non-tacky,	-
3	-	10	90	-	-	-	soft, tacky grease	-
4	-	10	-	-	-	90	firm, tacky grease	-
5	11.4	13.6	45.4	18.2	-	11.4	soft, slightly tacky, elastic putty	good
6	15	18	67	-	-	-	soft, non-tacky, non-elastic putty	-
7	-	25	-	-	75	-	soft, tacky, elastic putty; contains some lumps of copolymer	-

/1/ Weight percents shown are those charged and do not account
for any oils vaporized during fluxing.

/2/ Referred to as Special Plastic 153-2 in early reports.

very early work on sealants had shown considerable promise, sealant formulation was deemphasized in deference to the more pressing problems involved in lacquer formulation.

Much later in the program, several formulations were made up based on a low molecular weight modification of "KEL-F" Elastomer. In these formulations, the low molecular weight "KEL-F" Elastomer was heated with an equal weight of "KEL-F"-10 oil until a homogeneous mixture was obtained. The result was a clear, very soft, and tacky putty. The basic difficulty with this type putty was that the "KEL-F" Elastomer was too stiff to give a good putty except at high oil levels. At these high oil levels there were two disadvantages: (1) Such putties were extremely soft and tacky and (2) Increased amounts of oil in the formulation resulted in lowered WFNA resistance. Several attempts were made to cure this type of putty in the hope that a more firm sealant would result. The various cures attempted resulted only in cured masses of "KEL-F" Elastomer which separated from the bulk of the material. Nor was it possible to modify the "KEL-F" Elastomer sufficiently to obviate these difficulties.

At this time, sealant formulation work based on X-200 resin was begun. The early blends of finely divided X-200 resin and "KEL-F" oils showed considerable promise as WFNA resistant sealants. A typical formulation consisted of a 1:1 mixture of finely divided, off-spec. (i.e., ketone insoluble) X-200 and "KEL-F"-10 oil. The mixture was fluxed at 150°C. for 10-20 minutes to form a tacky, workable compound.

Concurrent formulation at U.S. Stoneware, involving the testing of a large number of resins and plasticizers which might be blended to form a WFNA resistant filleting compound, had shown that chlorinated materials such as Hypalon and Parlon show some promise, but that they could not compare with the fluorocarbons. A formulation similar to that described above using a mixture of X-200 and "KEL-F" oils resulted in a workable, adherent, WFNA resistant putty.

During the closing months of this contract, all the sealant formulation work was carried out at U.S. Stoneware. The reader is referred to their reports for detailed formulation and performance data. At the time of the termination of this contract, sufficient progress has been made to indicate that the sealants based on X-200 resin are superior in WFNA resistance to those based on any other resins. In addition, X-200 filleting compounds have good adhesion, minimum flow at 300°F., and remain putty-like after fluxing and temperature cycling.

V CURRENT SPECIFICATIONS FOR X-200 RESIN

Two grades or types of X-200 resin will be needed to meet the objectives of this contract:

A Lacquer Grade Resin

This resin must be completely soluble at 20% solids in methyl ethyl ketone, giving a solution with maximum clarity and a Gardner-Holt viscosity of B-D. (At the time of this writing, there is indication that resins having a maximum solution viscosity of J on the Gardner-Holt scale would be equally satisfactory.)

A Putty Grade Resin

This resin will be ketone-insoluble and largely soluble in tetrahydrofuran. To date, the resins used for sealant formulation have been those which were off-spec as lacquer resins. Since the main emphasis, both at Kellogg and at U.S. Stoneware, has been on lacquer resin and formulation, the specifications for a putty resin are not as firm as those for a lacquer resin. Through cooperation and exchange of information with U.S. Stoneware and WADC, it is expected that more rigid specifications can be written in the near future.

VI AVAILABILITY OF X-200 RESIN

Substantial quantities of X-200 resin will not be available until early in 1955 when a pilot unit, recently announced by the M.W. Kellogg Company, is scheduled for completion. Between March 31, 1954, the termination date of this contract, and January 1, 1955, the M.W. Kellogg Company has pledged its best efforts to supply 50 pounds of lacquer grade resin, "when and if available," against a U.S. Stoneware order. Meanwhile, cooperative evaluation with U.S. Stoneware of various lots of resin will continue.

VII APPENDIX A
APPARATUS AND TEST METHODS

N.S.T.; No Strength Temperature

This test constitutes a relative measure of molecular weight, although the relationship has not been fully defined for "KEL-F" copolymers. Please refer to Figure 3 for a diagram of the apparatus and a description of the method.

Intrinsic Viscosity

The intrinsic viscosity is the $\lim \eta_{sp}/C$ vs. C , as C approaches zero. In these tests, viscosities were determined for the polymer dissolved in 1, 1, 3-trifluoropentachloropropane at 210°F.

$$\eta_{sp} = \frac{\text{viscosity of the solution} - \text{viscosity of the solvent}}{\text{viscosity of the solvent}}$$

C = solution concentration in grams per 100 cc.

 T_m ; First Order Transition

T_m is defined as the temperature at which the polymer crystallites melt. It is determined by heating a pressed sheet of polymer in air and observing its optical properties between crossed polaroids. At T_m , the multi-colored crystals disappear.

Hardness

Shore D scale, ASTM D 676-49T, fifteen second reading.

Low Temperature Flexibility

Strips of plastic 3 in. x 0.5 in. x 0.010 in. are conditioned at -65°F. for four hours, then bent 180° around a 1/4 in. mandrel without being removed from the cold box. If the sample cracks, it fails the test.

Film Permeation Tests**a. Pfaudler Test for Supported Films**

Coated metal panels are exposed to both vapor and liquid in the standard Pfaudler cell. Failure is indicated by corrosion of the metal.

b. Unsupported Films

Two methods have been used to determine the resistance of unsupported X-200 films to permeation by WFMA:

NST -- No-Strength-Temperature -- TEST

This test was devised to provide a constant of relationship between various polymers and between polymers in various states, in lieu of molecular weights which are impractical to ascertain under normal circumstances. The test consists of determining the temperature Fahrenheit at which essentially all strength properties of any polymer are lost—a uniform sample size, sample thickness and weight strain being used for all tests.

"The measurement is carried out in the apparatus indicated at right. A $1\frac{5}{8}$ " x $\frac{1}{8}$ " x $1/16$ " strip is cut from a $1/16$ " sheet and symmetrically notched 1" from the end with a sharp punch so as to give a point of minimum cross-section of $1/16$ " x $3/64$ ". The sample is suspended vertically, as illustrated in the sketch, with a small weight attached to the 1" section of the test strip with a fine wire. The above mentioned weight is adjusted so that the total weight from the notch down is 0.5 gm. Starting at 420° F., the temperature is raised at the rate of 2.7° F. per minute until the sample pulls apart at the notch. The thermometer used is an ASTM -5° C. to +400° C. (23° F. to 752° F.), 76 mm. immersion.

The NST value is the temperature at which the test strip is pulled in two. This determination is not highly sensitive to small variations in test strip thickness (± 0.003 ") but care must be taken to cut a sharp clean notch. Differences of 10° F. are normally considered significant.

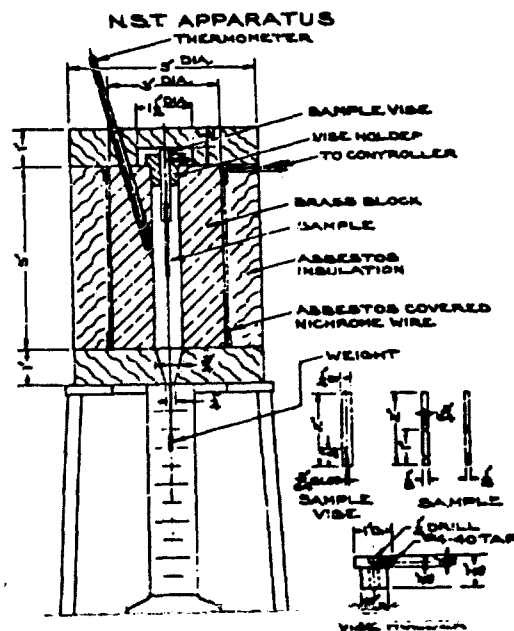


FIG. 3 NO STRENGTH TEMPERATURE TEST

Method 1. This method involves a new cell and procedure which were developed for this project. A diagram of the cell is shown in Figure 4. The test film is in contact with both liquid and vapor and is visible from both the front and the back. On the outside surface of the test film a thin layer of Watchung red (duPont RT-428-D) was deposited. The film was said to have failed when the dye was about one-half bleached by the acid. The bleaching reaction is rapid once vapors or liquid penetrate the film. Whenever possible, a protective "KEL-F" gasket was heat sealed to the exposed face of the film to prevent the glass cell edges from tearing the film.

Method 2. This method employs the HARTS H-cell. The cell is assembled using the X-200 test film as the diaphragm between the halves of the cell. One half of the cell is filled with the fuming nitric acid, and the other half is filled with distilled water. The film is said to have failed at the time that the pH on the water side of the film has decreased to 3.

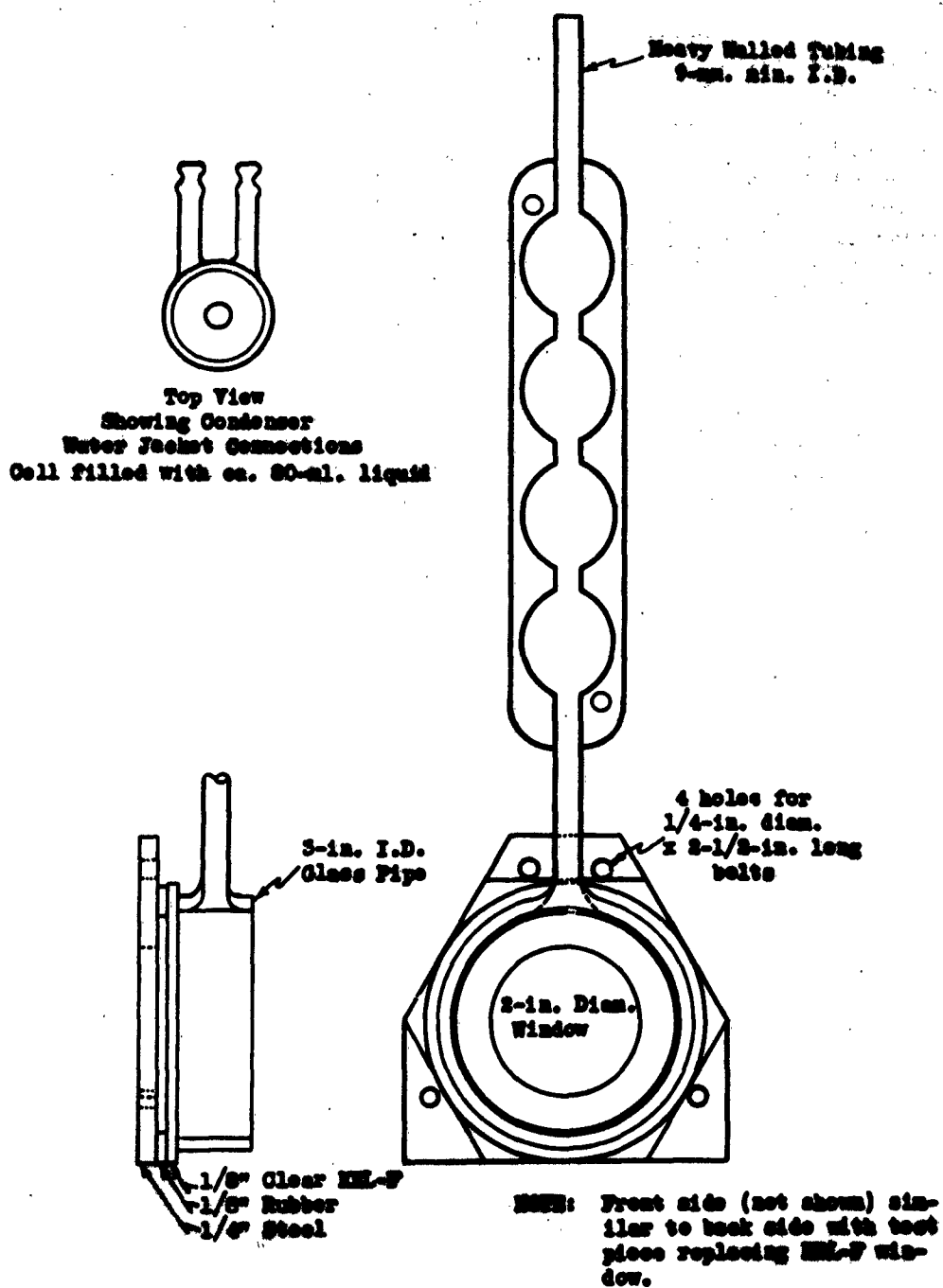


FIG. 4 TEST CELL FOR RESISTANCE OF "KEL-F"
FILMS TO CHEMICALS

VIII APPENDIX B
COPOLYMERS OF "KEL-F"

Exploratory Polymerization

When it became obvious that the $\text{CF}_2=\text{CFCl}$ homopolymer ("KEL-F") could not be applied to aircraft aluminum without injuring the mechanical properties of the metal, copolymerization of $\text{CF}_2=\text{CFCl}$ was undertaken as the next, most logical step. Comonomers selected for exploratory study were limited to those which are easily synthesized and having a high fluorine content: $\text{CF}_2=\text{CF}_2$, $\text{CF}_2=\text{CHF}$, and $\text{CF}_2=\text{CH}_2$. Initial plans called for the preparation of these $\text{CF}_2=\text{CFCl}/\text{X}$ copolymers at several levels of X, preferably 5-10-15-20 mole per cent.

The $\text{CF}_2=\text{CFCl}/\text{CF}_2=\text{CF}_2$ series was abandoned almost immediately because at no point from 0-100% $\text{CF}_2=\text{CFCl}$ does the product become soluble in common solvents at room temperature (see Table V for polymerization details).

The $\text{CF}_2=\text{CFCl}/\text{CF}_2=\text{CHF}$ system was also abandoned rather quickly because the yields were discouragingly low in a normally active polymerization recipe (see Table VI).

The $\text{CF}_2=\text{CFCl}/\text{CF}_2=\text{CH}_2$ system was far more encouraging. Polymerization was reasonably rapid, a wide range of copolymer composition was possible, and many of these copolymers were soluble in common solvents. Data on the polymerization of representative products at four $\text{CF}_2=\text{CFCl}/\text{CF}_2=\text{CH}_2$ levels are summarized in Table VII.

From previous work, it was known qualitatively that solubility of the $\text{CF}_2=\text{CFCl}/\text{CF}_2=\text{CH}_2$ copolymers would improve at higher levels of $\text{CF}_2=\text{CH}_2$, but that the products would become correspondingly less resistant to WFMA. It was necessary, therefore, to determine solubility and acid resistance quantitatively as a function of copolymer composition, so that these two key properties could be brought into balance in the ultimate product.

Accordingly, four batches of $\text{CF}_2=\text{CFCl}/\text{CF}_2=\text{CH}_2$ copolymers (designated as 917-B-1,2,4,5) were prepared by blending the products of a number of small-scale polymerization runs (similar to those in Table VII). These composite batches, ranging from 96/4 to 70/30 molar $\text{CF}_2=\text{CFCl}/\text{CF}_2=\text{CH}_2$, as well as "KEL-F", were checked for apparent molecular weight (NSI, intrinsic viscosity), first order transition temperature, hardness, low temperature flexibility, weight gain in WFMA at 125°F., and solubility in MEK and DIHK at 70° and 125°F. Results of these tests are shown in Table VIII. The acid resistance of blend 917-B-4 is compared with the resistance of several other coating and filleting materials in Table IX.

TABLE V
COPOLYMERIZATION OF $\text{CF}_2=\text{CFCl}(\text{KF})$ AND $\text{CF}_2=\text{CF}_2(\text{TFE})$

Run No.	Moles KF/TFE		Hours	% Conversion
	Charged	Found / l	Polymerization	
917-77	70/30	74/26	64	10
917-107	60/40	62/38	48	5
917-78	50/50	53/47	71	18
917-84	41/59	49/51	64	22
917-35	25/75	29/71	16	3

Recipe (parts by wt.): Monomers 100; $(\text{CCl}_3\text{COO})_2$ 0.0011; CFCl_3 < 0.8.

Temperature: -15°C .

Note: Polymerization procedures are described in Appendix B.

717 Duplicate F, Cl analyses.

TABLE VI
COPOLYMERIZATION OF $CF_2=CFCl(KF)$ AND $CF_2=CHF(TFE)$

Run No.	Moles KF/TFE		Hours Polymerization	% Conversion
	Charged	Found /l/		
917-76	70/30	84/16	114	3
917-80	60/40	81/19	120	8
917-104	40/60	63/37	451	4
917-82	31/69	53/47	209	7

Recipe (parts by wt.): Monomers 100; $(CCl_3COO)_2$ 0.0011; $CFCl_3$ <0.8.

Temperature: $-15^\circ C$.

/l/ Duplicate F, Cl analyses.

TABLE VII
COPOLYMERIZATION OF $CF_2=CFCl(KF)$ AND $CF_2=CH_2(VF_2)$

Run No.	Moles KF/VF_2		Hours Polymerization	% Conversion
	Charged	Found / l		
917-50	97/3	96/4	160	21
917-38	93/7	89/11	160	17
917-64	85/15	78/22	120	24
917-90	75/25	70/30	115	45

Recipe (parts by wt.): Monomers 100; $(CCl_3COO)_2$ 0.037; $CFCl_3$ < 0.8.

Temperature: $-15^\circ C$.

71/ Duplicate F, Cl analyses.

TABLE VIII
PROPERTIES OF "KEL-F" AND KELLOGG X-RESINS

	<u>"KEL-F"</u>	<u>Blend 917-B-2</u>	<u>Blend 917-B-1</u>	<u>Blend 917-B-4</u>	<u>Blend 917-B-5</u>
NST, °C.	240-330	327	303	319	315
Intrinsic Viscosity					
Powder	0.8-1.8	2.81	3.56	2.63	-
Pressed Film	0.8-1.8	1.88	2.60	2.37	-
First Order Transition T _m , °C.	211	195-202	156-167	115-117	
WFNA Resistance					
% Weight gain, 125°F.					
1 week	0.0	0.0	0.5	1.0	3.6
2 weeks	0.0	0.1	0.7	1.5	4.2
3 weeks	-	0.2	0.7	1.8	4.8
4 weeks	-	0.3	0.7	1.9	-
5 weeks	-	0.6	0.8	2.0	-
6 weeks	-	0.7	0.9	1.9	-
7 weeks	-	0.8	1.3	-	-
8 weeks	-	0.8	1.2	-	-
9 weeks	-	-	1.2	-	-
Soluble in Typical Lacquer Solvents (Ketones, Esters)	No	No	No	Yes	Yes
Hardness, Shore D	76	73	69	54	35
Cold Bend - 65°F.	OK	OK	OK	OK	OK

TABLE IX

WFNA RESISTANCE OF VARIOUS RESINS

Percent Weight Gain After Immersion in WFNA at 125°F.	Kellogg Blend 917-B-4	Veloform F-10		Fluoroline 100	Exon 400	Boeing Filleting Compound
		Pressed Sheet	Cast Film			
1 week	1.0	109	34	94	46	disintegrates
2 weeks	1.5	-	-	-	-	-
3 weeks	1.8	-	-	-	-	-
4 weeks	1.9	-	-	-	-	-
5 weeks	2.0	-	-	-	-	-
6 weeks	1.9	-	-	-	-	-
7 weeks	-	-	-	-	-	-
8 weeks	-	-	-	-	-	-
9 weeks	-	-	-	-	-	-

It is apparent from Tables VIII and IX and from Figures 5 and 6 that the copolymer designated as 917-B-4 represents the best balance of solubility and acid resistance of all the resins tested. There are some (notably "KEL-F" and copolymers 917-B-1,2) which have slightly better WFNA resistance, but these resins are not soluble at room temperature in common lacquer solvents. Copolymer 917-B-5, on the other hand, offers no advantage over 917-B-4 in solubility and is less acid resistant. All the experimental copolymers, as a class, are far more WFNA resistant than the other proposed resins, namely, Veloform F-10, Exon 400, Fluoroline 100. This conclusion is illustrated not only by data in Table IX but by the photographs in Figures 5 and 6.

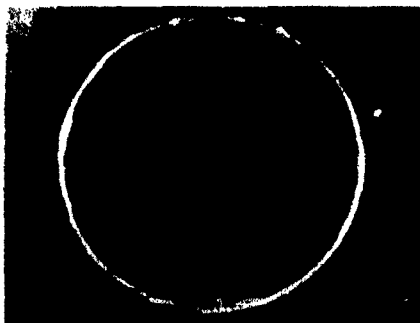
Copolymerization of $\text{CF}_2=\text{CFCl}$ and $\text{CF}_2=\text{CH}_2$

Since the tests described in the previous section indicated that copolymers of the type represented by batch 917-B-4 were soluble in lacquer solvents without sacrificing WFNA resistance, this copolymer system was selected for suspension copolymerization studies. Suspension polymerization was to be favored over the peroxide-catalyzed mass polymerization system for several reasons: (1) The former system would afford easier handling and the possibility of good yields in hours rather than in days as required in mass polymerization. (2) A suspension polymerization system would be easier to scale-up to a production level. (3) Greater latitude and control of reaction conditions would be possible with a suspension system.

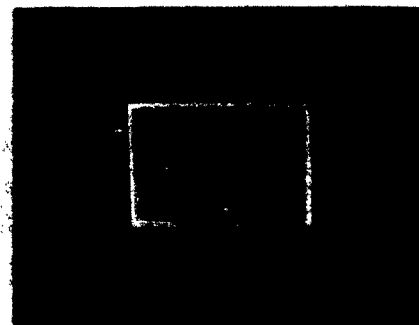
The basic suspension copolymerization recipe chosen was a persulfate-bisulfite system. Typical recipes along with the resins resulting from several of the early polymerizations are summarized in Table X. Although these resins were insoluble in ketones, they were sufficiently soluble in tetrahydrofuran (THF) to allow some preliminary lacquer formulation work. Despite the fact that THF is an acceptable lacquer solvent, it was felt that our objective should still be a ketone soluble resin having sufficiently high chlorotrifluoroethylene content to impart excellent WFNA resistance.

It is significant to note that resins having a $\text{CF}_2=\text{CH}_2$ content as high as 36 mole percent (see number 737G, Table X) made by suspension polymerization were ketone insoluble. Earlier resins made by mass polymerization at -15°C . were ketone soluble when the $\text{CF}_2=\text{CH}_2$ content exceeded 22 mole percent. Since the most probable explanation for this ketone insolubility seemed to be excessive molecular weight, suitable modifiers were sought for the suspension recipe.

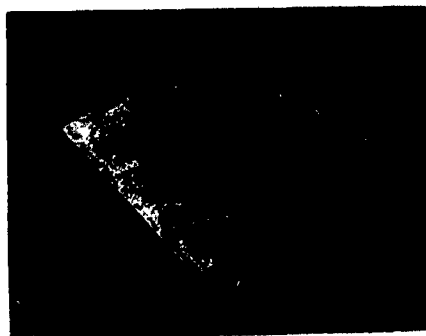
BEFORE

KELLOGG
RESINBlend
917-B-4

AFTER



EXON-4



FLUOROLINE-100



FIG. 5 EFFECT OF WHITE FUMING NITRIC
ACID AT 125° F.

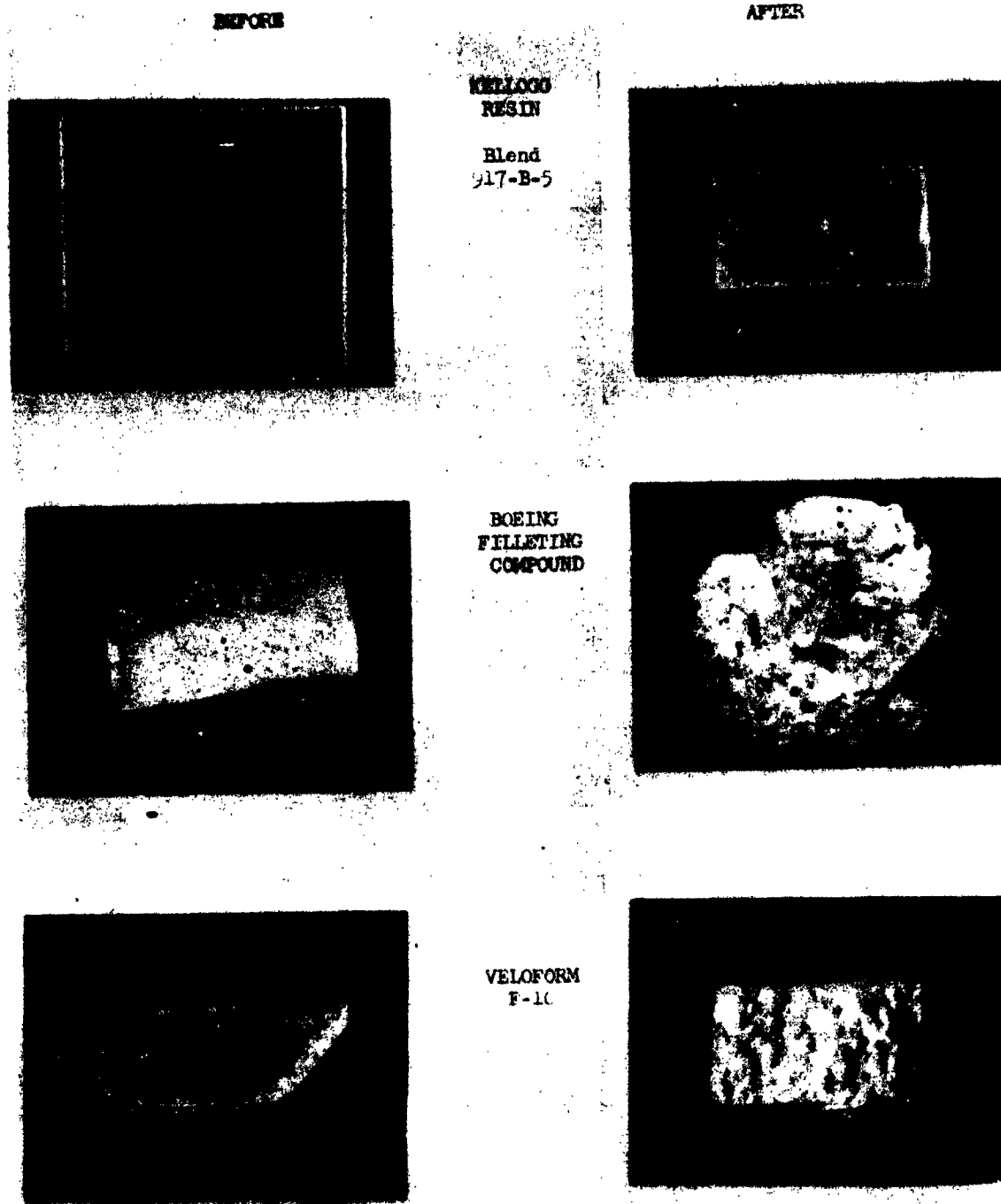


FIG. 6 EFFECT OF WHITE FUMING NITRIC
ACID AT 125° F.

TABLE X
SUSPENSION COPOLYMERIZATION OF $\text{CF}_2=\text{CFCl}$ AND $\text{CF}_2=\text{CH}_2$

Run Number	745	758	761	762	687G	737G	785G
Recipe, pts. by wt.							
Water	200	200	200	200	200	200	200
$\text{CF}_2=\text{CFCl}$	94.2	89.1	94.2	94.2	92.2	86.5	87.8
$\text{CF}_2=\text{CH}_2$	5.8	8.9	5.8	5.8	7.8	13.5	12.2
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	1.0	1.0	1.5	2.0	2.0	1.0	1.5
$\text{Na}_2\text{S}_2\text{O}_5$	0.4	0.4	0.6	0.8	0.8	0.4	0.6
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.05	0.05	0.075	0.10	0.2	0.1	0.15
Monomer ratio, moles	90/10	85/15	90/10	90/10	86/14	78/22	80/20
% Conversion	14	22	22	22	27	24	54
Molar ratio combined, $\text{CF}_2=\text{CFCl}/\text{CF}_2=\text{CH}_2$	78/22	70/30	75/25	82/18	75/25	64/36	76/24
Soluble in MEK at Room Temperature?	No	No	No	No	No	No	No

A rather large number of compounds was studied to determine their effect as modifiers on the suspension copolymerization. Of all the compounds studied, chloroform (CHCl_3) most effectively modified the copolymerization. Table XI compares unmodified recipes with those modified with chloroform at various monomer ratios. Here we note that chloroform effectively lowers the relative molecular weight (as measured by the solution viscosity) resulting in increased ketone solubility at a given monomer ratio.

In the thought that $\text{CF}_2=\text{CFCl}$ monomer might remain absorbed on the resin particles long enough to form ketone insoluble polymer, several runs were made in which the copolymerization was short-stopped. This was accomplished by rapidly venting the excess monomers from the reactor at the end of the reaction period and immediately treating the polymer with acetone to remove any absorbed monomer. The results of several of the more promising runs carried out in this manner are summarized in Table XII. Here we see that this technique results in more readily ketone dissolved polymer; however, this improvement is generally at the expense of lowered yields.

The next approach was an attempt to minimize ketone insolubility by controlling the charge ratio as well as limiting the conversion in a chloroform modified, suspension recipe. That this approach was quite successful is shown in Table XIII. Here one notes that ketone soluble copolymer can be made with relatively high conversion using the suspension recipe number two.

Essentially, this completes the summary of our copolymerization studies at the time of termination of this contract. We are quite optimistic that ketone soluble copolymers, containing sufficiently high levels of monochlorotrifluoroethylene to be WFNA resistant, can be made using a chloroform-modified, suspension system. We also believe that there will be sufficient interest in this resin to warrant a continuation of this work. Therefore, the suspension copolymerization will be studied further on a larger than laboratory scale for the twofold purpose of further delineating optimum reaction conditions and of supplying sufficient amounts of copolymer for both lacquer and putty formulations.

TABLE XI

EFFECT OF MODIFIERS ON THE SUSPENSION COPOLYMERIZATION /1/ OF

 $\text{CF}_2=\text{CFCl}$ AND $\text{CF}_2=\text{CH}_2$

Run	Molar Charge Ratio, KF/VF_2	Modifier	Parts Modifier	% Conversion	Mole % KF in Polymer	Solubility in MEK	Viscosity, /2/ cs.
789	86/14	none	-	99	80	insoluble	1.18
790	90/10	none	-	94	86	"	1.02
791	80/20	none	-	95	80	"	1.23
795	86/14	CHCl_3	10	49	78	10% soluble	0.55
796	90/10	CHCl_3	10	6	83	insoluble	0.53
797	80/20	CHCl_3	10	54	71	20% soluble	0.98

/1/ Standard 20°C. Suspension Recipe: Water 200; monomers 100; $(\text{NH}_4)_2\text{S}_2\text{O}_8$ 1.0;
 MgSO_4 0.4; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.1

/2/ Dilute solution viscosity at 130°C. and 0.5% solids.

TABLE XII
EFFECT OF SHORT-STOPPING THE
COPOLYMERIZATION OF $CF_2=CFCl$ AND $CF_2=CH_2$

Run Number	930G	959G	960G	973G
Moles KF/VF_2 charged	82/18	82/18	85/15	85/15
Polymerization time, hrs.	4	7	6	17
Polymerization temp., °C.	20	20	20	15
% Conversion	4	6	7	21
Soluble in MEK?	YES	YES	YES	YES

Recipe (parts by weight): Water 200; monomers 100; $(NH_4)_2S_2O_8$ 1.0;
 $Na_2S_2O_5$ 0.4; $FeSO_4 \cdot 7H_2O$ 0.05; $CHCl_3$ 10
 (except in 930G).

Shortstop: Acetone

TABLE XIII

RECENT CHLOROFORM MODIFIED COPOLYMERIZATIONS

Run No.	Moles Charged $\text{CF}_2=\text{CFCl}/\text{CF}_2=\text{CH}_2$	Recipe	Modifier, Parts CHCl_3	Polymerization		% Conversion	Moles Combined $\text{CF}_2=\text{CFCl}/\text{CF}_2=\text{CH}_2$	MEX Solubility
				Time, Hrs.	Temp., °C.			
975G	82/18	1	10	17	15	23	76/24	soluble
977G	"	1	10	18	20	11	75/25	"
978G	"	1	10	19	20	16	79/21	"
979G	"	1	10	19	15	24	81/19	insoluble
980G	80/20	1	10	19	15	25	68/32	soluble
986G	"	1	10	19	15	24	67/33	"
992G	76/24	2	10	20	15	39	75/25	"
1001G	"	2	10	20	15	35	-	insoluble
1002G	"	2	10	20	15	40	76/24	soluble
1003G	"	2	10	20	15	39	72/28	"
1019	"	2	10	20	15	40	70/30	"

Recipe 1 (parts by weight): Water 200, monomers 100, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ 1.0, $\text{Na}_2\text{S}_2\text{O}_5$ 0.4, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.05.

Recipe 2 (parts by weight): Water 200, monomers 100, " 2.0, " 0.8, " 0.1.

IX APPENDIX C
POLYMERIZATION PROCEDURE

It has been general practice to carry out exploratory copolymerization with a total weight of 5 g. of the monomer mixture. These polymerizations are conducted in heavy-walled, Pyrex tubes which have a capacity of about 20 ml. In the X-200 copolymerizations, where monomers were readily available and larger amounts of the polymer were desired, 300 ml. tubes were used. If the pressures involved were unduly high, a stainless steel reaction vessel was employed which had a capacity of about 300 ml. Such a steel vessel is available from American Instrument Company, Silver Spring, Maryland, and is known as a micro reaction vessel. It requires a shaking mechanism and heating jacket as auxiliary equipment.

The following experimental directions apply to the copolymerization as carried out in 300 ml. glass tubes, using as an example the chloroform-modified suspension recipe (Recipe 1, Table XIII). The procedure is essentially the same when the Aminco bomb is used. When polymerization is carried out in a 300 ml. reactor, 50% of the recipe taken in grams is used (for example: 100 g. of water, 50 g. of mixed monomers, etc.).

Clean, 300 ml., heavy-walled, Pyrex tubes are flushed with nitrogen by alternately evacuating and filling them with gaseous nitrogen on a suitable vacuum manifold system. As soon as each tube is removed from the manifold, it is quickly stoppered.

The tube is charged by adding 50 ml. of water (deionized) solution containing 0.5 g. of ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$). The tube is then placed in a freezing bath consisting of a slush of dry-ice and trichloroethylene. When the contents of the tube are frozen solid, a solution of 0.2 g. of sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) in 25 ml. of deionized water is added. The contents of the tube are again frozen, and a solution of 0.025 g. of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in 25 ml. of water and 5 g. of chloroform modifier added successively, repeating the freezing operation after each addition. The tubes are then stored in the freezing mixture until it is desired to add the monomers.

The monomers employed are gases at room temperature. To charge such monomers to the polymerization tubes, a glass vacuum manifold system is employed. This system has inlets where monomer tanks may be connected, a gaseous nitrogen inlet, a connection for a polymerization tube and a standard-taper joint into which glass graduated cylinders of various sizes may be fitted. The manifold may be opened to the atmosphere; it is equipped with a vacuum pressure gage and is connected to a vacuum pump. Various sections of the manifold system may be isolated from each other.

To add the gaseous monomers, the tube containing the frozen catalysts is connected to the manifold, quickly evacuated, and then immersed in liquid nitrogen. The monomer tanks are then connected to the manifold. The "KEL-F" monomer ($\text{CF}_2=\text{CFCl}$) is added to the polymerization tube by first condensing it in a graduated cylinder connected to the manifold and cooled in Dry-Ice and trichloroethylene. The density of $\text{CF}_2=\text{CFCl}$ at the temperature of the cooling bath is known; therefore, it is possible to calculate the weight of the monomer condensed in the graduate from the measured volume. The required amount of $\text{CF}_2=\text{CFCl}$ is then distilled under vacuum into the previously evacuated polymerization tube by removing the Dry-Ice-trichloroethylene bath followed by warming the outside of the graduate with a stream of water, if necessary.

The more volatile vinylidene fluoride does not condense at the temperature of the Dry-Ice-trichloroethylene bath. This monomer may be condensed if a liquid nitrogen bath is used around the graduate. Although solid monomer separates at this temperature and weights calculated from densities and volumes under these conditions are probably somewhat in error, the method is rapid and for this reason has been used frequently.

An alternate way of handling the more volatile $\text{CF}_2=\text{CH}_2$ involves the condensation of an excess of the monomer required with liquid nitrogen, followed by the transfer of it to an evacuated measuring flask of known volume. If the pressure is noted, the flask closed off, and the system evacuated, one has a sample, in excess of what is needed, at a known pressure, temperature and volume. One can transfer from this sample until the pressure in the measuring flask falls to a value found by calculation to correspond to the excess. The flask is closed off, the monomer remaining in the system allowed to condense into the polymerization tube, and the excess in the flask vented.

When both monomers are in the polymerization tube and thoroughly frozen with liquid nitrogen, the tube is filled to atmospheric pressure with gaseous nitrogen. The manifold is then opened to the atmosphere, and a small stream of nitrogen gas is passed through it and the attached polymerization tube. The liquid nitrogen bath in which the polymerization tube was immersed is now removed, and the gaseous nitrogen stream through the system is shut off. The neck of the tube is quickly drawn to a point where the passage-way through it is approximately of capillary size. The liquid nitrogen bath is carefully replaced about the tube after the manifold opening to the atmosphere is closed. When the contents of the tube are thoroughly cooled by the bath, the tube is evacuated; the bath is again removed, and the tube sealed off at the point where it was drawn down.

Polymerization is carried out by tumbling the tubes for the desired time in a water bath whose temperature can be automatically maintained at $20^{\circ}\text{C.} \pm 1^{\circ}\text{C.}$ The tumbling is accomplished by fastening the tubes, enclosed in metal jackets, to the circumference of a rotating metal wheel. The wheel is mounted on a horizontal shaft in a water bath and rotated at a constant rate by an electric motor. The wheel is completely immersed except for a small sector at the top.

When the polymerization period is over, the tubes are removed and placed horizontally in pulverized Dry-Ice. If extremely low-boiling monomers are present, the tubes are then further frozen in liquid nitrogen. The tops of the frozen tubes are broken off to release pressure, and a scratch is made with a file on the side of each tube, just below the shoulder. The tube is grasped with both hands (heavy asbestos gloves are used) and broken by striking on the edge of the bench. With care, no product is lost. The bottom half of the broken tube is clamped in an inverted position over a stout container, extending as far into the container as possible. The monomers escape as the tube warms up and eventually the contents are forced out. The latter operation is dangerous because trapped monomers may cause the tube to burst; it should be carried out behind a shield.

The residual polymer is then washed from the tubes with water. The freezing operation generally coagulates all the polymer, but filtration is often difficult. Heating the suspension to boiling increases the rate of filtration. Frequently, simple decantation of the supernatant liquid is the most satisfactory way to separate the coagulated polymer from its mother liquor. The polymer is then washed several times with water.

The polymers are dried to constant weight in a vacuum oven at 35°C. Analyses for chlorine or fluorine or both are obtained and the mole per cent of each monomer in the polymer calculated from these analyses. If both a chlorine and fluorine analysis are obtained, the value reported for the mole per cent monomer in polymer is an average of the values calculated from chlorine and fluorine analyses.